EXHIBIT M

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APPENDIX H: METHODOLOGIES FOR BATTERY FAILURE ANALYSIS

Quinn Horn, Troy Hayes, Daren Slee, Kevin White, John Harmon, Ramesh Godithi, Ming Wu, Marcus Megerle, Surendra Singh, and Celina Mikolajczak

Exhibit
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H.1. *INTRODUCTION*

As rapidly advancing battery technology drives new and expanded battery applications in areas such as consumer electronics, toys, electric and hybrid vehicles, and medical devices, interest in ways to determine the causes of battery failures and preventing these failures has increased. Batteries can fail in a variety of ways, including loss of capacity and/or rate capability, short circuit, loss of case integrity, and thermal runaway, among others. Often a given root cause of failure can result in a range of other battery behaviors. For example, electrode contamination within battery cells typically results in poor battery performance due to capacity fade, but in certain instances contamination may also result in cell thermal runaway reactions. The severity of a given failure is dictated by the specific battery chemistry, battery size/capacity, physical construction of the battery, and criticality of its application. Flammability and chemical and thermal stability of battery components vary with cell chemistry; the amount of energy that can be released varies with cell size (e.g., a short circuit of an automotive battery is likely to have greater safety implications than a short circuit of a AAA alkaline cell). The acceptability of differing levels of "failures" varies with the battery application (e.g., loss of capacity may be considered a relatively benign failure in a cell phone application, but may be considered a critical failure in a medical device application).

Failure analysis of battery systems is a multidisciplinary endeavor that generally requires an understanding of:

- Fundamental battery chemistry

- Physical cell design and construction

- Electronic protection systems

- Cell, battery, and battery pack manufacturing processes

For example, in some cases, lithium-ion battery failures may be induced by external forces such as severe mechanical damage or exposure to fire, while in others they may be the result of problems involving charge, discharge, and/or battery protection circuitry design and implementation. In still other cases, field failures may be caused by internal cell faults that result from rare and/or subtle manufacturing problems. The fact that batteries can fail on rare occasion in an uncontrolled manner due to manufacturing defects has brought an increased public awareness for battery safety as a result of two recent very large product recalls of portable computer batteries.[1-4]

It is beyond the scope of this appendix to discuss the full range of possible battery failures, even for a single chemistry. However, any failure can be investigated effectively by using thorough scientific methodologies, including collection of observations and evidence, development of a hypothesis, and the testing of that hypothesis. This appendix describes a number of techniques that can be used as part of the investigative process, with particular emphasis on how to make observations and form a failure mode hypothesis. Testing to recreate a failure can be readily conducted to assess a hypothesis in some cases; however, often complete testing to recreate a failure is not practical and the failure mode hypothesis will rest solely on collected observations and limited test results. The techniques and conclusions presented in this appendix are intended as guidelines for how to approach a battery failure analysis. Most battery failure investigations do not require the use of all of the techniques discussed here. Furthermore, it should be noted that each battery failure is a special case and thus requires a unique combination of various investigative strategies and techniques that should be tailored for that specific investigation accordingly. Due to current interest in lithium-ion batteries, many examples in this appendix are drawn from failure analyses of lithium-ion cells. Further discussion of lithium-ion battery failures can be found in the literature.[5-18]

H.2. *COLLECTION OF BACKGROUND INFORMATION*

When a battery failure occurs, information useful to the investigation can generally be collected from the end-user as well as from the incident site. Ideally, the user can provide information on the device background, usage history, and the failure symptoms or a description of the failure incident. Useful information may include:

- Length of time the battery had been in service

- Typical usage environment (hot, cold, humid, vibration) and any significant excursions from normal conditions

- Extenuating factors such as liquid spills, dropped systems, mechanical shocks (rapid accelerations/ decelerations), rapid electrical discharges, thermal shocks, or recent repair activities

- Behavior of the system leading up to the time of the incident (i.e., nominal or atypical system performance)

- State of the system at the time of the incident (plugged in or not, for how long, on or off)

- Symptoms of failure or observations during or after an incident

- Actions in response to the failure or incident

- Descriptions of any injuries, and their severity, that occurred due to the incident

- Photographs of the scene

Of course, such user accounts can only be used as a reference and may not always be entirely accurate; however, when combined with analysis of the incident evidence, user accounts may provide useful information about the nature of the incident. Systematic inspection of the incident site and careful documentation of the surroundings of the physical evidence present an opportunity to gather valuable information. Any observed damage patterns (thermal, mechanical, electrical, or chemical) should be evaluated for consistency with the described incident and product involved.

NFPA 921, "Guide for Fire and Explosion Investigations," provides a recognized guide for the investigation of fire and explosion sites, and objects involved at such scenes.[19] The general techniques described in this guide can be applied to investigate a wide range of battery failures, even in instances where a fire or explosion has not occurred. Though conducting an investigation as described in NFPA 921 is preferred, it is often not possible because the site may have already been cleaned up or significantly altered by the time the investigation begins. Photographs provided by the end-user or other investigators, if any, should be examined carefully for evidence of factors that might have contributed to a battery failure.

H.2.1. Recovery of Physical Evidence or Samples

Physical objects identified as important to establishing the cause of a battery failure may be, or may eventually become, evidence in a legal proceeding and must be handled appropriately. ASTM E1188 provides guidelines for evidence collection, handling, and preservation.[20] Guidelines for labeling physical evidence and related documentation are provided in ASTM E1459.[21] If a failure is energetic, parts may become separated during the incident itself or after the failure due to the activities of fire or clean-up crews. The investigator should make an effort to retrieve all the cells, printed circuit boards, and components associated with an incident battery, as well as other items that might be related to the cause of the failure if possible (e.g., sources of heat, power, or fuel and any other objects that were damaged during the incident). Sometimes chips or other components of the battery protection circuitry are ejected from the battery pack during an incident so it is important to carefully check the scene for any loose components.

Destructive examination of a battery, or any examination of a battery after a failure, may pose safety or health hazards that need to be identified and mitigated through engineering controls or selection of appropriate personal protective equipment. For example, a battery case rupture may result in leakage of cell electrolyte or active materials, which can irritate the skin, eyes, or respiratory system. In a failed multicell battery, such as found in a notebook computer or electric vehicle, some cells might have reacted while other cells are damaged but remain fully charged and possibly susceptible to shorting. A comprehensive list of potential hazards associated with all cell chemistries and battery types is beyond the scope of this appendix. The investigator should develop a safety plan prior to disturbing, shipping, or conducting a destructive examination of any battery or its associated system. Material safety data sheets (MSDS) as well as regulatory agency websites (EPA, NIOSH, OSHA, etc.) can provide data to use in developing a safety plan.

A failed system or battery pack may not comply with international (e.g., IATA, ICAO, IMO) and U.S. Department of Transportation (DOT) shipping exemptions for normal battery packs. Depending upon its condition, a failed system or battery may need to be treated as hazardous material for shipping purposes. In some instances, it may not be possible to ship the failed sample necessitating on-site examination. Personnel certified according to U.S. DOT Hazardous Material Training are required for declaring, labeling, packaging, and shipping hazardous materials in the United States. Similarly, the battery may need to be stored as a hazardous material prior to or after examination. For example, a damaged battery may need to be stored in appropriate chemical or flammability cabinets, or vented cabinets, or biohazard bags. National or local regulations may apply. Finally, battery components may need to be disposed of as hazardous waste, per national or local regulations, subsequent to an investigation.

Host Device or System Examination

Nondestructive Visual Examination. When investigating apparent battery-related failures, the host device or system (phone, notebook computer, toy, electric vehicle, etc.) should be examined. If available, the host device or system should be thoroughly documented in the as-received condition and prior to any alteration, including photographing from all sides and perspectives. Careful attention should be directed to areas that exhibit visual damage patterns or other abnormalities such as mechanical deformation, signs of enclosure breach, soot deposits, regions of charring, melting, cell swelling, electrolyte leakage, locations of electrical activity (including arcing), as well as signs of exposure to environmental elements, such as liquid or foreign contaminant intrusion. These patterns can help the investigator determine the orientation and state of the host device or system at the time of the incident. For example, an examination of a power cord and the device's power inlet port may indicate whether it was plugged into the unit at the time of an incident. If examining a flip-type cell phone, notebook computer, or any other device that can be opened and closed, the incident unit should be opened, if possible without causing damage, so the screen and other internal components (keyboard, touchpad, etc.) can be examined and photographed. Witness marks in the form of heat damage or smoke patterns will generally indicate whether the unit was opened or closed at the time of the incident. Caution should be used in interpretation of such evidence, as users may alter the state of the device as the incident is occurring. For example, a notebook computer may be closed and moved to a different location after a user observes the initial stages of a thermal runaway incident. Device and battery pack serial numbers should be noted for possible later follow-up with manufacturers. This often involves significant effort in cases where severe damage has occurred, but can be critical when the root cause is related to manufacturing defects.

Reconstruction. If an incident host device or battery is not intact or fully assembled upon initiation of the failure analysis, the investigator should attempt to reconstruct the system, if possible, by placing the appropriate parts into their original location(s) and/or orientation as much as possible without introducing any additional damage or altering the condition of the evidence (Fig. H.1). This, along with comparison to an exemplar device, will allow for a better understanding of possible damage propagation. This is necessary, for instance, when batteries have experienced failures that caused one or more cells to separate from the system during an incident. Such reconstruction efforts often involve detailed analysis of connecting tabs in comparison with exemplars. Caution is needed during this process, however, as some tabs may shift during an incident (e.g., the cap of an 18650 lithium-ion cell may rotate during an incident and become fixed in a new orientation upon cooling).

Figure H.1 *Portion of a failed battery pack made up of 18650 lithium-ion cells. (Courtesy of Exponent, Inc.)*

System and Battery X-Ray. After a visual examination and possible reconstruction, the battery and system should be examined using x-ray imaging, if practical, to further document the evidence nondestructively. X-ray examination of the battery and/or system may provide insight into the relative positioning of components as well as damage propagation. X-ray imaging may also allow characterization of the extent and distribution of circuitry and electrode damage, if present. If practical, both the incident system and battery should be x-rayed in their fully assembled condition (e.g., for smaller systems such as notebook computers, MP3 players, or DVD players). X-ray images should be taken at different viewing angles to allow for a complete view of the assembled battery and the system. The x-ray images should be examined closely for internal damage to the battery and battery protection circuitry or other anomalies. Although these components may be examined in more detail upon subsequent disassembly, the overall view of the damage pattern and physical relationship between the damaged cells and surrounding parts generally offers important clues as to the initiation point(s) of the failure and the sequence of any propagating events. An example of a thermal runaway propagation in a multiple-cell configuration is shown in Fig. H.2. This figure shows the effect of cell venting (from the cell cap) onto the windings of an adjacent cell. On a more practical level, x-ray imaging can also provide guidance on how to disassemble a host device or battery for further examination without compromising key internal components.

Figure H.2 X-ray image of part of a lithium-ion battery pack. The effect of cell venting from a cell cap on the windings of an adjacent cell can be observed, as indicated by the arrow. (Courtesy of Exponent, Inc.)
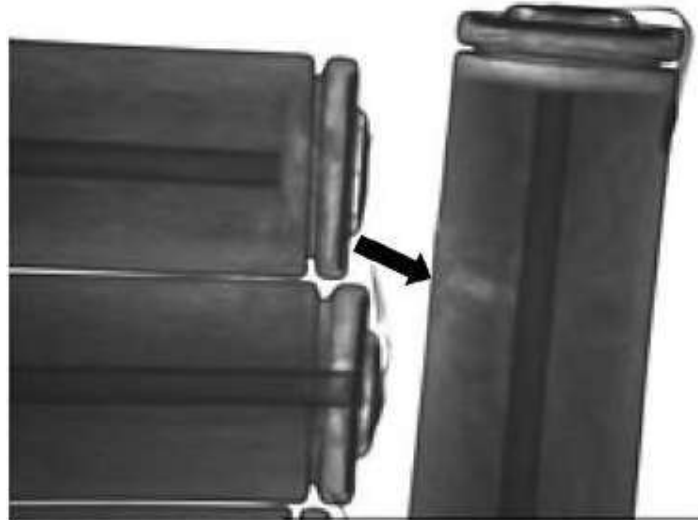
Status and Functionality Tests. If a battery failure is nonenergetic, the host system is often undamaged and can be tested with an exemplar battery pack or various electronic loads. With certain types of battery failures (for example, loss of capacity), the battery itself may be tested. Even if a failure is energetic, a host system may remain functional even though it appears damaged. It is also possible when a system is not functional to harvest functional components for testing, as these systems or components may provide status or incident-related information or allow for selected functionality tests. Host device operating parameters of particular importance related to battery functionality, reliability, and safety include charge and discharge voltage and current cutoff points, overvoltage, undervoltage, overcurrent, and low and high temperature cutoff points. For multiplecell in-series applications, block[*] voltage sense points, and cell or block imbalance and rebalancing schemes, as well as locations of multiple temperature sensing points, may also be of interest. Further, the condition of fuses and other printed circuit board components may be relevant depending on the failure mode.

Investigators should familiarize themselves with the operational characteristics of the host device or system prior to energizing any components if such testing is attempted. Familiarity can be obtained by reviewing product and component literature, including circuit schematics, or by examining and characterizing the operating parameters of an exemplar host device or system experimentally. If there is concern that energizing the host device may result in a change of state or damage to some components, every effort should be made to gather all possible data before attempting to energize the system. For example, volatile registers on EEPROMs will likely be altered upon re-energizing a host device and subsequently obtained data would not necessarily reflect the condition at the time of the incident.

H.3. *BATTERY AND CELL EXAMINATION*

To determine the cause of a failure it is generally necessary to open a damaged battery pack, extract and examine the remains of the cells, the battery protection printed circuit board(s) (PCBs), and any fuses or thermal cutoff devices. This examination is destructive and should only be conducted after all appropriate parties have been contacted, and an examination of the overall pack, x-rays, and/or an examination of an exemplar unit has been made to minimize the likelihood of damage to key components during the incident investigation.

The disassembly process should be conducted carefully and methodically with any abnormalities noted and documented. For example, during the disassembly of one incident unit, evidence was found that it had been previously disassembled and rendered inoperable by that process. This observation, in combination with heat and burn patterns indicating an external flame attack, suggested the incident was likely the result of a deliberate attempt by the user to cause the battery failure intentionally.

Once the battery pack case has been removed to expose the cells, the appearance of the cells should be documented and the cells uniquely marked for future identification. Markings should include sufficient detail to define cell orientation for reference during subsequent analyses. It is also important to determine the electrical configuration of battery cells in a multiple-cell pack to identify the different voltage levels present at the terminals of each battery cell. While still connected, if possible, in-circuit cell-block voltages and impedances should be measured. Close attention should be given to the electrical path throughout the pack, starting from the external pack connector to the cells. The focus should be on identifying signs of potential inadvertent short-circuit points between cells and wires or battery tabs and connections that may have resulted in a failure of the pack.

A determination ultimately must be made if any observed damage or anomalies are part of the failure root cause or are consistent with follow-up events after the initiating failures. For example, soft pouch lithium-ion polymer cells can leak electrolyte, resulting in shorting of pack protection electronics. Cell leakage in this example—which can be caused by improper sealing, direct mechanical damage of the pouch during pack assembly, corrosion of the pouch resulting from improper pouch isolation during cell manufacture, etc.—is the root cause of the failure rather than the observed shorting on the protection PCB.

After an in-circuit examination, cells should be disconnected from the protection PCB and then from each other. Care should be taken when removing cells to avoid any damage to the cell case or electrodes. If any damage occurs during cell extraction, this damage should be documented so that it is not considered during the development of a failure mode hypothesis. When dealing with the disassembly of multicell lithium-ion systems, it is important to cut the connecting wires or metal tabs in the order of highest to lowest potential, preventing the possibility of opening fuses or causing other damage to the cells and the protection PCB. This approach is also typically the safest way to handle potentially charged cells. Insulation on cells and connecting wires may have been compromised during an incident, and thus additional care should be used to minimize the risk of creating an external short circuit while handling the cells (e.g., with cutting tools).

Once cells have been separated, they should be examined and photographically documented. It is particularly important to find and record any cell serial numbers. Cell serial numbers normally include a date code for cell manufacture (which sometimes can be traced back to particular manufacturing lines or batches). This information can be used by the cell manufacturer to retrieve data about the production history of particular cell lots, and used to identify exemplar cells from the same date code for follow-up examinations. Such information can help identify whether the observed failure resulted from a systematic manufacturing problem or was an isolated event. In addition, should a cell recall become warranted, cell date codes can be critical in helping to bound the population of cells to be recalled.

Cell cases or pouches should be examined visually for signs of mechanical deformation. Magnifiers and optical microscopes are often useful for this type of examination. Denting a cell case may create immediate or delayed shorting resulting in a loss of performance or possibly subsequent thermal runaway of the cell. Dents created during battery pack assembly processes that ultimately led to cell failures have been observed with lithium-ion polymer soft pouch cells. Note, however, that dents in cells that have undergone energetic reactions are often created by post-incident handling (e.g., extinguishing a fire, collecting and shipping the remains). In addition, not all preexisting cell case dents result in cell failure, as most cells are robust to certain amounts of deformation. Before a failure can be attributed to pre-incident mechanical damage, evidence must be found that the dent caused damage to and/or shorting of cell windings. This is generally done through examination of cell x-rays, CT scans (discussed later), or by opening the cell and directly examining the windings.

The voltages, weights, and impedances of the individual cells should be measured at 1 kHz. These measurements can help determine whether a cell lost electrolyte, whether internal protections activated, whether the cell separator was heat damaged, and/or the state-of-charge at the time of the failure. Cells can then be examined with nondestructive techniques such as x-ray and CT scanning. As part of the overall failure analysis, nominally operational incident or exemplar cells may be subjected to a variety of electrochemical diagnostic techniques, including cell cycling and electro-chemical impedance spectroscopy. Subsequent destructive physical analysis (DPA) of operational or nonoperational cells can include reference electrode testing (on operational cells only), cell gas sampling and analysis, cell disassembly, and cell cross-sectioning.

H.3.1. Cell X-Rays

If cells have been visibly damaged, or if internal cell faults are suspected, detailed x-ray (and/or CT scan, discussed below) examination of the cells should be made. Typically, it is useful to examine cells (and record x-ray images) at two or more planes or at different angles depending on the cell type, particularly in regions of winding disturbances. X-ray images showing the cell from the plan view (orientation as seen from above when battery pack is laid flat) are useful in observing the effects of potential interactions between adjacent cells. Analysis of detailed x-ray images is often crucial in determining the sequence of thermal runaway (in a multicell lithium-ion pack), determining the initiating cell in a thermal runaway incident, and developing a theory for the cause(s) of the initial cell failure.

For example, the electrode windings of an 18650 model lithium-ion cell that initiates a failure in a multicell pack often appear comparatively lightly damaged in x-ray images, while the windings of cells that reacted later show sites of greater damage, including resolidified globules throughout those cells. Little melt damage occurs in the initiating cell because this cell is at or near the ambient operating temperature when it begins developing a short circuit. Much of the energy from this cell can be consumed by the shorting event itself and in self-heating to the critical temperature where thermal runaway occurs. Once the separator melts, there is less energy left in the cell to cause additional pronounced shorting. The reaction of the initiating cell increases the temperature of neighboring cells. The separators of these cells consequently melt due to external heating, while these cells are still at or near their initial state of charge. This results in substantial shorting (melting) throughout the cell and an overall greater degree of internal damage. In cases where a catastrophic failure induces rapid thermal runaway (e.g., from a puncture to a cell in a pack from an external source, external heating of the battery pack, or overcharge of the cell), the initiating cell may be the most heavily damaged cell. Maximum damage occurs to the initiating cell here because the shorting and subsequent thermal runaway are so rapid they often result in ejection or partial ejection of the cell windings. Neighboring cells are heated more gradually before going into thermal runaway and may not experience the same level of internal damage as the initiating cell.

X-ray images showing all the internal leads in profile and the alignment of all cell windings near the cell ends are also generally useful. Malformed leads and misaligned windings have been shown to lead to internal cell failures. These types of manufacturing defects can be caused by problems with the machinery used to assemble cells, and if so, occur repeatedly, to various degrees of severity, in cells manufactured within the same time frame. Thus, even if these features are no longer visible in reacted cells (as a result of melting or deformation during cell venting), examining nonreacted cells from the same time frame can be helpful in identifying whether a manufacturing problem exists.

H.3.2. Computed Tomography Scanning

In computed tomography (CT) scanning, x-rays are taken along a line rather than being integrated through the entire volume of the object. An image representing a planar slice of the object is then reconstructed by mathematically combining data from multiple x-rays taken in the same plane but at different angles. The set of resulting images provides a three-dimensional view of the cell interior rather than an averaged image containing information from all of the material and components along the path between the x-ray source and detector, as in traditional planar x-ray. In the reconstructed CT scan images, high-density regions appear bright, while low-density regions appear dark (the reverse of a traditional x-ray image). For example, in a typical 18650 lithium-ion cell, the copper current collector appears as a thin bright line, the cobalt oxide cathode appears as a thicker gray line, and the graphite appears as a black line between the copper current collector and cobalt oxide cathode (Fig. H.3). A high-resolution CT scan of an 18650 cylindrical cell will consist of approximately 1000 slices. The resulting slice thickness of each scan cross section would be 70 μm with an in-plane resolution of approximately 20 × 20 μm. Once CT data have been collected, they can be reprocessed to generate a cross-sectional image along any desired object plane. Figure H.4 shows a longitudinal cross-sectional image generated from CT scanning data of an 18650 cell subjected to a crush test that ultimately resulted in cell thermal runaway. The cell was originally scanned in the same manner as the cell in Fig. H.3.

The application of CT scanning to examination of a failure in a particular cell chemistry and format is mainly limited by the following considerations: size of the imaging chamber, strength of the x-ray source, cell geometry, and cell materials. Since CT scanning is a dynamic process requiring movement of the sample within a chamber, larger samples will necessitate a larger chamber. Larger format cells or cells containing denser materials will require a higher-power x-ray source. If the x-ray source is not strong enough, it will result in an image where the edges of the object might be resolved, but the interior portions of the cell are not. The best CT scan images are obtained for cells with symmetrical geometries (e.g., cylindrical cells) as a result of the image reconstruction algorithm. As cell geometries become more asymmetric, image blurring and severe shadowing can occur. The amount and location of image blurring and shadowing will be related to the degree of asymmetry of the sample being scanned. When imaging materials with large differences in density (e.g., lithium adjacent to steel), it is possible that the lighter material will not appear in the reconstructed image. Prismatic and other similar form factors may be scanned in sections multiple times along different axes to decrease the asymmetry of the scanned portion of the cell and increase the scanning resolution of the entire cell. For example, a 50 mm wide cell may be scanned using two offset axes as two 25 mm wide cells.

Figure H.3 A single CT scan cross-sectional image from a commercial 18650 cylindrical cell. (Courtesy of Exponent, Inc.)
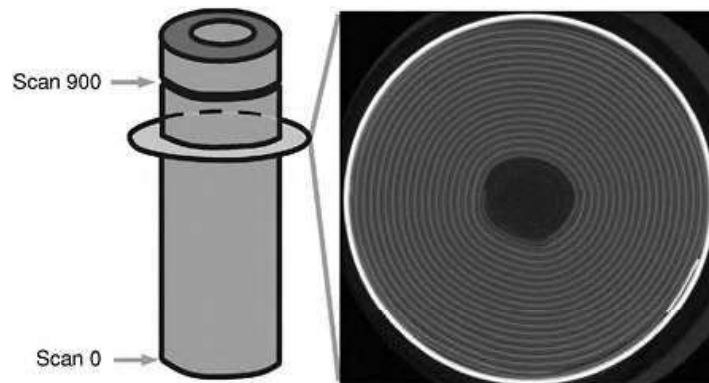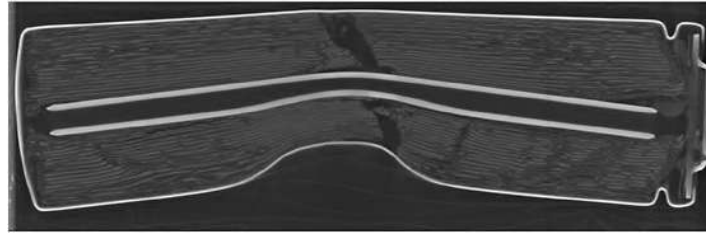
Figure H.4 CT scan cross-sectional image of a crushed cylindrical 18650 lithium-ion cell that subsequently underwent a thermal runaway reaction. (Courtesy of Exponent, Inc.)

CT scanning can be a powerful nondestructive diagnostic tool for evaluating the internal structure of batteries that is complementary to planar x-ray. While planar x-ray examination can quickly and effectively screen out some defects such as tab shape/positioning and global electrode misalignment with a single image, it is limited in its ability to screen for localized defects, even when significant numbers of planar x-rays are taken of a single cell, because of the masking effect created by the inherent image averaging that occurs. In general, CT scanning is more effective in identifying contaminant particles or other point defects that may be lost during averaging over an entire cell. The ability to detect contaminant particles by CT scan increases as the atomic number of the contaminant increases and as the difference between the atomic number of the contaminant and the surrounding materials increases. CT scans can also show whether internal windings might be misaligned, distorted, torn, or melted, identify points of electrode delamination or cracking, identify areas of extra or missing material, show whether cell enclosure corrosion has occurred or whether a lithium-ion cell has experienced severe overdischarge (copper-dissolution), and reveal a variety of internal defects that may otherwise go undetected by planar x-ray.

When examining a lithium-ion battery pack that has undergone thermal runaway, traditional planar x-ray should be used in the preliminary portion of the examination as discussed. If the failure appears to have been caused by an internal cell fault, planar x-rays can be used to identify the cells most likely to have initiated the reaction. Once the likely initiating cells have been identified, further nondestructive examination can be conducted using CT scanning prior to cell disassembly. CT scanning is particularly useful for wound cylindrical lithium-ion cells that have experienced significant damage upon thermal runaway and cell venting, so that cell unrolling is not possible.

Example

Example: CT Scanning of Primary Cells.

Failure analysis and general examination of primary cells pose a number of challenges, especially for lithium primary cells, which must be opened in the inert atmosphere of a glove box if lithium metal, or a corrosive and/or volatile cathode material, is to be examined. Such disassembly also requires appropriate engineering and personal protective equipment. In addition, though disassembly will reveal surface features on components, it will not reveal hidden subsurface voids or cracks in the components. CT scanning allows for the inspection of individual components and features within the cell, such as current collectors, active material interfaces, cell leads, void spaces, and cracks. It can also be used to examine electrode alignment and positioning, detect internal case pitting and corrosion, visualize the uniformity and shape of the sealing surfaces, and assess overall cell construction quality.

To demonstrate the applicability of CT scanning on primary cells, a variety of cells of different constructions at various states of charge were scanned. Figures H.5 and H.6 present a CR2050 lithium/manganese dioxide primary coin cell at the fully charged and discharged states, respectively. The overall cell construction is clearly visible, including the press fit steel exterior, sealing surfaces, cathode pellet, and metallic lithium anode. The steel exterior corresponds to the brighter portions of the image. The manganese dioxide cathode is the gray region within the cell interior. The apparent gradation change in image density in the manganese dioxide in the CT images is an artifact of the imaging process due to a larger volume fraction of steel from the cell exterior being located toward the image top. Materials with low x-ray absorbance, such as the lithium metal anode or void spaces, will appear black in a CT image. For instance, in Figs. H.5 and H.6, the lithium metal anode is the black region directly below the cathode.

Figure H.5 CT scan cross-sectional image through the center of a CR2050 lithium/manganese dioxide primary cell (~100% SOC). (Courtesy of Exponent, Inc.)

Figure H.6 CT scan cross-sectional image through the center of a CR2050 discharged lithium/manganese dioxide primary cell (~0% SOC). (Courtesy of Exponent, Inc.)

The interface between the cathode material and anode is clearly visible, and its location was tracked versus the discharge state of the cell. Figure H.6 shows the same cell in the nominally discharged state. As would be expected, the lithium has been almost entirely consumed, which is seen as a decrease in the imaged black region within the cell. A concomitant swelling of the cathode matrix was observed due to intercalation of the lithium. Furthermore, fractures that developed within the cathode material due to swelling (dark lines through the cathode material) are shown in Fig. H.6. Similar fracturing of the cathode material upon cell discharge has been observed in other cells in the discharged state and does not necessarily represent a cell design or manufacturing defect as long as cell performance and safety are not impacted by that fracturing.

Figure H.7 is a CT image of the internal construction of a CR1/3N lithium/manganese dioxide primary cell at 50% state of charge (SOC). The cell has a spiral-wound construction utilizing wire mesh current collectors. The metallic parts, such as the steel can, metallic wire mesh electrodes, and center pin, appear as bright regions within the image. The cathode material corresponds to the gray regions within the image. The lithium metal corresponds to the black regions adjacent to the cathode material. The sealing surfaces are visible within the figure and appear to indicate a relatively uniform gasket compression with no signs of corrosion. The lithium metal has been consumed unevenly during discharge. This is clearly demonstrated in the image where the lithium metal has an uneven interface with the cathode active material. Additionally, voids and fractures are evident throughout the cell. The voids are coincident with the current collector mesh. Fractures of the cathode active material appear to propagate outward from those voids along the cathode active material current collector interface. This observation coupled with isolated voids adjacent to the current collector tends to indicate void formation occurs first, followed by fracturing of the cathode active material matrix as intercalation of the lithium into the manganese dioxide progresses during discharge.

Figure H.7 CT scan cross-sectional image through the center of a CR1/3N lithium/manganese dioxide primary cell (50% SOC). (Courtesy of Exponent, Inc.)
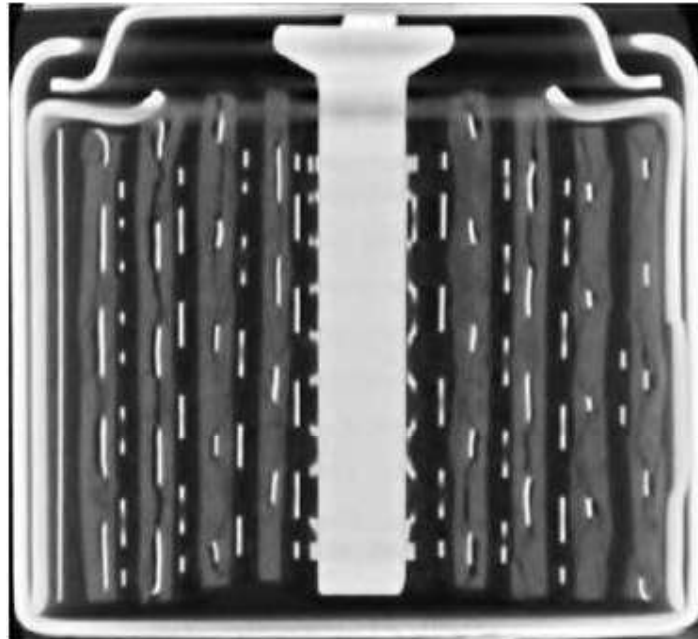
Figure H.8 shows a CT scan image of a 9 V alkaline zinc/manganese dioxide cell. There are six cells in series in alternating orientations within the battery (this cross section shows three of the cells). The zinc powder particles in the anode are clearly visible within the image. It is also apparent that the distribution of zinc is not uniform throughout the cells. There are irregularities along the anode/cathode interface as a result of folds and creases in the separator. Other features that are clearly illustrated include anode pin alignment, cell wall uniformity/integrity, and distribution of anode and cathode active materials.

H.3.3. Cell Gas Sampling and Analysis

The active materials of most battery chemistries are capable of facilitating the conversion of condensed phase materials to gases. In some instances, the generation of gas is part of the normal operation of the electrochemical couple. The electrolysis of water from the electrolyte of a lead-acid cell during the final stages of charging is an example of normal gas generation. In other instances, gas generation is a direct indication that undesirable chemical and/or electrochemical reactions of the cell components are occurring. For example, in lithium-ion cells some generation of light hydrocarbon gases can occur during normal operation due to the kinetically hindered reaction of electrolyte components with the active materials of the cell. However, large scale generation of gaseous by-products that may cause cell swelling or venting is an indication of degradation of cell components. As a result, analysis of gases generated in lithiumion cells is often a powerful tool for understanding the reactions that may have generated them and, subsequently, the specific failure mode that a cell may be experiencing.

Gas chromatography/mass spectroscopy (GC/ MS) is most often chosen as the analytical technique for the analysis of gases generated in failed cells. GC/MS allows for the separation and quantitative identification of the gas sample components and often provides the information necessary to determine the origin of the gas generation. Because GC/ MS is inherently sensitive, sample collection and storage prior to testing are critical for maintaining the integrity of the sample and preventing erroneous data due to the introduction of contaminants. Gas-tight syringes, equipped with nonreactive seal materials and a valve mechanism to retain the sample within the barrel of the syringe, are effective collection and sample storage tools.

Figure H.8 CT scan cross-sectional image through three cells in a 9 V alkaline Zn/MnO$_2$ primary battery (100% SOC).
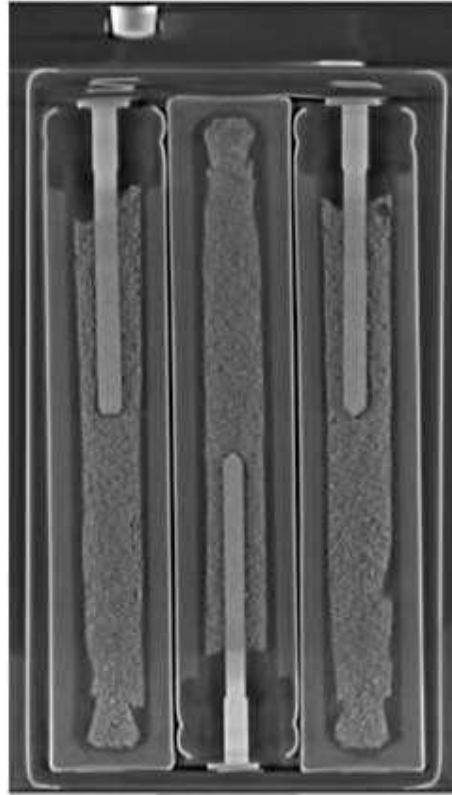
Cell construction and form factor play important roles in the method chosen for the collection of a gas sample from a failed lithium-ion cell. Gas collection from a swollen pouch-type cell is easily achieved by forcing a syringe needle through a septum adhered to the exterior of the cell. If a typical noncoring syringe needle is used, the septum thickness should be greater than the length of the needle bevel to avoid introduction of the environment outside the cell. Cells with hard cases that are not easily punctured by a needle of a syringe provide additional challenges to collecting uncontaminated samples. Not only must a method be developed to penetrate the cell without allowing the escape of the desired gases or contamination by ambient gases, the investigator must identify a location in the cell where a syringe needle can be inserted without short-circuiting the electrode windings and contaminating the gas sample through the generation of gas not related to the original failure. It is often necessary to perform x-ray or CT imaging of the cell to identify a suitable cell location for needle insertion, and then fabricate sampling apparatus designed to facilitate needle placement and gas sampling.

The gases generated in a cell will depend upon the materials used in the construction of the cell, and in the case of cell contamination, the gases generated are additionally dependent on reactivity of the foreign material. Correct interpretation of gas analysis results requires knowledge of the electrode material types, the composition of the electrolyte solvent, and the identity of the electrolyte salt and electrolyte additives. Additionally, an understanding of the most probable chemical pathways for reactive material degradation is necessary to realize the full benefit of generated gas analysis.

In lithium-ion cells, gas generation can often be assigned to one of three general causes:

- Overcharge of the active materials
- Overdischarge of the active materials
- The presence of contaminants in the cell

Working with a graphite/LiCoO$_2$ cell system, Kumai et al.[22] developed guidelines for interpreting gas composition during overcharge and overdischarge processes. In general:

- Overcharge produces conditions in which oxidative degradation pathways for reactive cell components dominate the gas generation mechanisms.

- Overdischarge produces conditions in which reductive degradation pathways for reactive cell components dominate the gas generation mechanisms.

For example, a gas sample collected from an overcharged 18650 cell[*] consisted of a complex mixture of gases, a major component of which was CO$_2$. CO$_2$ is an oxidized form of carbon that is likely due to the oxidation of the electrolyte at the positive electrode surface facilitated by the evolution of oxygen from degrading positive electrode material. The following chemical equations describe the degradation of the positive electrode and the subsequent oxidation of the electrolyte to form CO$_2$:

$LiCoC_2 \rightarrow Li_{0.5}CoO_2 + 1/2Li^+ + 1/2e^-$	(normal charge reaction)
$Li_{0.5}CoO_2 \rightarrow CoO_2 + 1/2Li^+ + 1/2e^-$	(overcharge reaction)
$3CoO_2 \rightarrow Co_3O_4 + O_2$ (gas)	(positive material degradation and O$_2$ evolution)
Electrolyte + $3O_2$ (gas) $\rightarrow 3CO_2$ (gas) + H$_2$O	(electrolyte oxidation)

While not reported by Kumai et al., the presence of hydrogen in a failed lithium-ion cell is an indicator of overcharge that is the product of reactive material reduction within the cell. On overcharge, lithium metal can be deposited at the negative electrode. This highly reducing metal reacts with the electrolyte to produce hydrogen and various electrolyte reduction products.[23] The detection of hydrogen is a particularly useful indicator of overcharge as the probability of its generation in the absence of lithium metal is low.

H.3.4. Cell Disassembly

Cell disassembly can be accomplished in a variety of ways, depending upon the goals of the examination. The most commonly used approach is a cell "unrolling" or "destacking" where the cell case is removed and the windings are either unrolled (wound cells) or separated (prismatic cells) and examined. This is an important step when trying to identify a specific point of failure in reacted cells or manufacturing defects in exemplar cells. Cell unrolling or destacking generally allows examination of all surviving electrode and separator surfaces, as well as the condition of various tabs, welds, insulators, internal protection devices, and the cell case or pouch. The cells can be documented and examined throughout the process of disassembly using high-resolution digital photography, stereomicroscopy, and scanning electron microscopy (SEM) as appropriate. Care should be taken to document any damage introduced to the windings by the disassembly process.

Opening any cell, particularly one that is partially charged (e.g., a lithium-ion cell at 3 V) or fully charged (e.g., a lithium primary cell) presents a number of safety hazards, and should only be attempted after the investigator has developed a thorough understanding of the cell design and chemistry, a safety plan for the process, including appropriate engineering controls (fume hood, glove box), appropriate personal protective equipment (gloves, goggles, apron, respirator), a contingency plan for handling a cell should it become shorted during the disassembly process and begin to self-heat (containment, fire extinguishers, bucket of sand in which to submerge a shorted cell), and a plan for storage and disposal of cell components. The investigator should consider the potential hazards associated with the cell components, including toxicity and potential flammability (hydrocarbon-based electrolytes, lithium metal, etc.). Examination of cell x-rays, CT scans, or engineering drawings is recommended when planning cuts in cell cases. Nonconductive or insulated tools are recommended, but even nonconductive tools can cause shorting if they bring electrodes of opposite polarity together.

Figure H.9 *Photograph showing the initial stages of the examination of electrode and separator surfaces of an 18650 lithium-ion cell. (Courtesy of Exponent, Inc.)*

In the case of very high-energy cells, such as lithium-thionyl chloride, the cell should be frozen in liquid nitrogen and then allowed to thaw partially before disassembly.

Example

Example: Lithium-Ion Cells.

For lithium-ion cells that have not undergone thermal runaway reaction, cell unrolling (Fig. H.9) or destacking can reveal the presence of contaminants, microshorts (Fig. H.10), and areas of lithium plating (Fig. H.11) on electrode surfaces and separators. Internal leads, welds, insulators, and regions of tape can also be examined for anomalies (Figs. H.12 and H.13).

For lithium-ion cells that have undergone thermal runaway, destruction of not just the cell separator, but melting of the aluminum current collector has likely occurred. In such cases, failure analysis proceeds with detailed examination of the remaining negative electrode (anode) material, particularly the copper current collector, which generally remains mechanically intact. Such examination often reveals the presence of holes in the copper current collector at a variety of different locations and with different character. Figure H.14 is a simplified schematic of a post– hermal runaway copper current collector, depicting representative locations of several types of holes observed.

Single or small clusters of holes surrounded by evidence of melted and resolidified copper are often observed. This type of hole, or cluster of holes, will generally be isolated from other holes on the current collector. It is generally found in areas of the winding where both copper and aluminum current collectors were coated with active material, rather than in regions of bare copper current collector. Often it will be surrounded by and even partially obscured by remaining active material coating. The edges of this type of hole will often show clearly defined ridges or lips with relatively smooth features (Fig. H.15). Furthermore, there are often nodules observed extending into the holes. In each case, the edges of the hole exhibit rounded features and are generally thicker than the original current collector. This indicates that the copper has undergone a change in shape to decrease the surface energy by minimizing the surface area, a change that can only occur by melting. Hence, it is evident that the copper current collector was locally melted and subsequently resolidified. These regions do not exhibit alloying with aluminum, which can be confirmed by scanning electron microscopy and energy dispersive spectroscopy (SEM/EDS).

Figure H.10 Photographs showing evidence of a microshort on a separator (top) and associated anode material (bottom) observed during disassembly of a lithium-ion cell. (Courtesy of Exponent, Inc.)
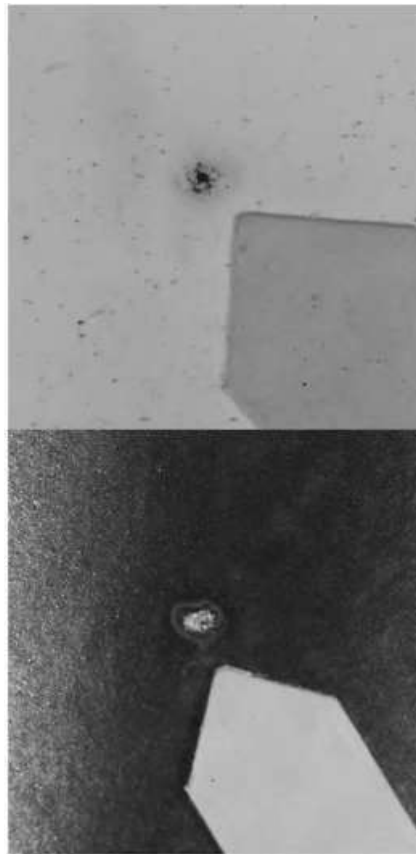
Though many features can be observed on surviving current collectors after thermal runaway, holes surrounded by resolidified copper likely have special significance. Cell skin temperatures measured during induced thermal runaway reactions do not approach the melting point of copper (1357 K). Holes surrounded by resolidified copper rarely form in more than one cell of a battery pack that has undergone an accidental thermal runaway reaction in the field in the absence of cell overcharge for cells with capacities of ~2200 mAh or less. This suggests that uniform external heating of a cell, which causes large areas of the separator to melt simultaneously, is unlikely to produce regions of melted copper. The very limited areas of observed copper melting indicate brief, localized energy transfers consistent with electric faulting. Such faulting could only occur while most of the cell separator is neither melted nor shrunk, and while a sufficiently conductive path exists to the copper current collector (for example, for a soft pack cell, before heating of the electrolyte has caused gas generation and separation of the electrode layers). Such a feature may, therefore, be indicative of the point or area within a cell that initiated the thermal runaway event. Caution needs to be exercised in such an interpretation, however, because a weak point within a cell (e.g., contaminant, corner in the case of a flat or prismatic cell, etc.) can result in preferential softening and shorting during the heating of a cell from other causes (a different origination point or external heat attack). In addition, for cases where a cell is overcharged, or for cells with higher initial capacities, the energy remaining within the cell after an initial shorting event may be sufficient to cause follow-up shorting events at multiple locations in a cell.

Figure H.11 *Photograph showing evidence of lithium plating on the surface of the negative electrode removed from a discharged lithium-ion cell. In the presence of water vapor, white foam will form at locations of plated lithium due to the generation of lithium hydroxide and hydrogen gas. (Courtesy of Exponent, Inc.)*

Figure H.12 Photograph showing indications of corrosion on the interior, bottom surface of the cell can from an 18650-size lithium-ion cell. (Courtesy of Exponent, Inc.)
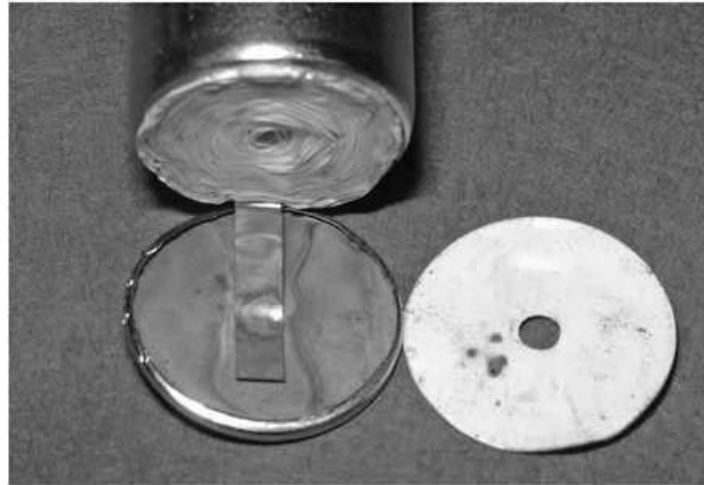
Figure H.13 Photograph of the cell cap assembly from an 18650-size lithium-ion cell showing evidence of a metal burr on the cathode lead edge (circled). (Courtesy of Exponent, Inc.)

Figure H.14 Simplified schematic of a post–thermal runaway copper current collector from a wound prismatic cell depicting typical locations of damage: (1) hole surrounded by resolidified copper found in region of active material, (2) regions of copper aluminum alloying near anode lead tab and venting areas, (3) tear in current collector. (Courtesy of Exponent, Inc.)
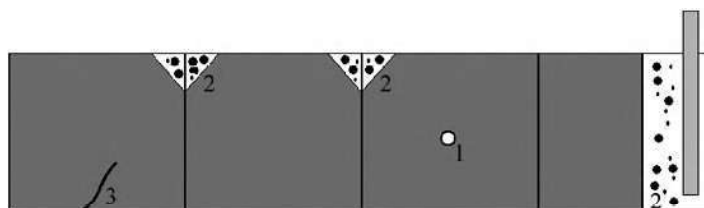
The copper current collector of a lithium-ion cell that has undergone thermal runaway will typically exhibit many holes, only a few, if any, of which are surrounded by evidence of resolidified copper as described above. Typically, the majority of holes are the result of alloying between copper and aluminum. When liquid aluminum contacts copper metal, it forms a low melting point eutectic mixture, which subsequently melts or oxidizes and forms holes.[24] Alloying holes are typically observed with higher frequency in regions of the copper current collector where melted aluminum could most easily pool onto bare copper, such as:

1. Areas where the copper has not been coated with active material, such as in the region of the anode lead or ends of the windings, which is adjacent to an area of uncoated aluminum current collector.

2. Along the edges of windings where melted aluminum can pool or collect during a thermal runaway event.

3. In the vicinity of a cell vent port, where passage of heated gases and the presence of oxygen result in damage to the active material coating of the copper current collector. Note that vent pathways will depend upon cell geometry, construction, and surrounding geometry of the host device, as well as the dynamics of the thermal runaway event.

Figure H.15 Stereo-microscope image showing an example of a hole with a clearly defined melt front/ridge (arrows) from resolidified copper. (Courtesy of Exponent, Inc.)

Despite the presence of liquid aluminum during thermal runaway, and evidence that liquid aluminum can be transported throughout the cell—cells that have undergone thermal runaway often exhibit small beads of resolidified aluminum near vent ports or electrode edges (Fig. H.16)—most active material coated regions of copper current collector do not generally exhibit alloying with aluminum. Either the liquid aluminum does not wet the anode material (graphite) and as such is unable to penetrate the anode coating, or liquid aluminum is wicked into the anode and cathode coatings, thus segregating it from the copper current collector. Mercury porosimetry measurements of commercially produced cells indicate porosity of 25 to 30% in active material coatings. In our experience, a typical ratio of aluminum current collector thickness to cathode active material coating thickness (single side) is on the order of 1:4. Thus the two layers of cathode active material surrounding the aluminum current collector should be able to accommodate all of the locally melted aluminum and thereby keep it away from the copper current collector. Indeed, the fact that cells which have undergone thermal runaway can be opened and often unwound to reveal smooth layers of anode active material is a strong indication that liquid aluminum generally does not infiltrate the anode active material. As a result, regions of alloying not associated with vent paths or bare copper may be an indication of damage or flaking to the active material coatings prior to thermal runaway.

Figure H.16 Photograph of an 18650-size lithium-ion cell showing beads of resolidified aluminum visible at edge of cell winding after cell thermal runaway. (Courtesy of Exponent, Inc.)
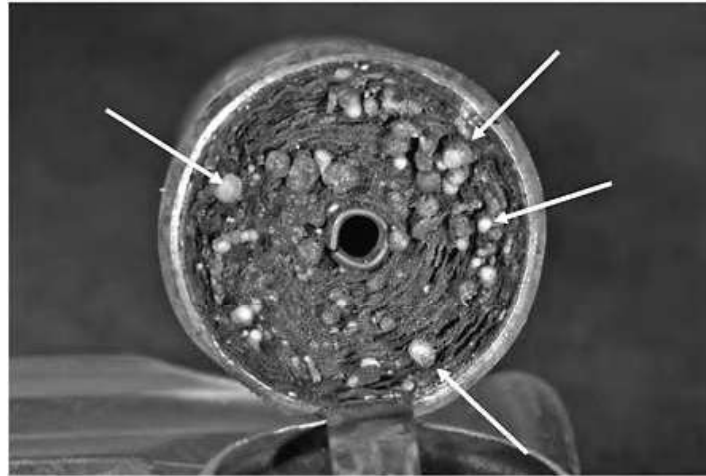

The edges of alloying holes tend to either be lined with a brittle, oxidized gray-metallic material (an oxidized aluminum-copper alloy), a darker halo where the material has alloyed but not melted or oxidized, or a clean sharp copper surface where the alloy has detached from the remaining unaffected copper (like a punched-out hole). Alloyed regions of aluminum and copper are clearly visible when examined with SEM imaging using backscattered electron contrast. In this mode, higher atomic number materials such as copper appear brighter, while lower atomic number materials such as aluminum appear darker.[*] In a backscattered SEM image, holes created by alloying will tend to have a halo or darkened edges compared to the brighter appearance of the bulk of the current collector. This darkened region is associated with Al-Cu alloying.

During pack and cell disassembly, it is often difficult to avoid mechanically tearing or disturbing the heat-exposed cell windings. If the anode is torn after thermal runaway, it will exhibit relatively clean surfaces surrounding the damaged areas. Anode tears made prior to thermal runaway are subjected to elevated temperatures, vent gases, and possible alloying with aluminum. Consequently, such tears may exhibit heat patterns and other signs of elevated temperatures. Sometimes a tear will be associated with a hole surrounded by evidence of copper melting and resolidification.

On occasion, evidence of contamination is observed on post–thermal runaway copper current collectors. For evidence of foreign material to survive the thermal runaway process and be detectable, the contaminant must have contained materials not normally associated with either the anode or cathode. For detection after cell opening, the contaminants would generally have to have been splattered or alloyed onto the anode or the copper current collector and not been consumed or displaced. As a result, though it is possible to detect the presence of non-native species, particularly metallic contaminants, it is generally not possible to directly detect the presence of plastic, aluminum, or copper contaminants. In fact, it is rather uncommon to find any evidence of contamination when examining melt holes in the copper current collector.

Figure H.17 CT scan of an 18650 lithium-ion cell subjected to severe overdischarge resulting in copper dissolution and the formation of fine holes in the copper current collector, particularly in the circled regions (thermal runaway did not occur). (Courtesy of Exponent, Inc.)
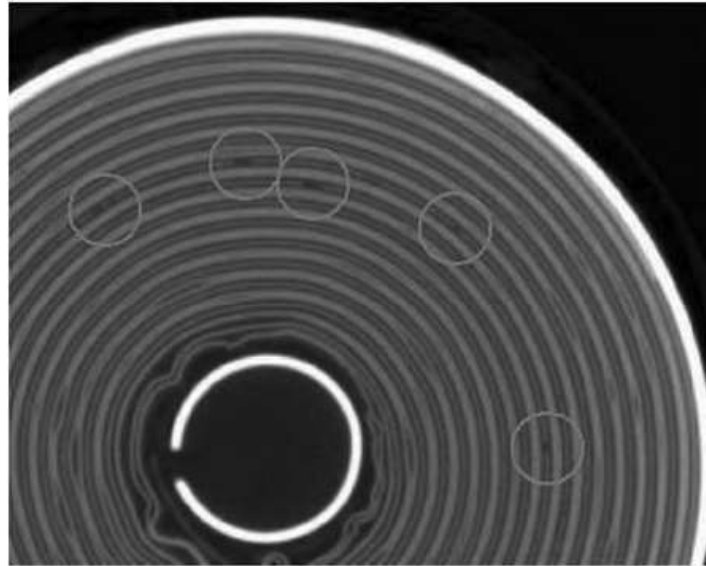
Cell overdischarge may cause copper dissolution to the point where numerous small holes form in the copper current collector. Figure H.17 is a CT scan cross section of an 18650-type cell that was subjected to severe overdischarge (but has not undergone thermal runaway). In this image, the copper current collector appears as a thin bright line and the aluminum coated with cobalt oxide appears as a thicker gray line. In places throughout the cell, the copper current collector appears discontinuous—broken by a series of small holes, with diameters in the plane of the cross section on the order of the current collector thickness. These types of holes have been found to be the result of copper dissolution. Figure H.18 shows one of these types of holes upon unrolling of a cell that has not undergone thermal runaway. The hole diameter here is on the order of the thickness of the coated anode layer.

Upon recharge of a cell that has undergone overdischarge, copper is deposited on the anode material, causing degradation of that material. This can lead to lithium plating on the anode and possibly thermal runaway of the cell. If a cell that has experienced overdischarge and thermal runaway is opened and unwound, close examination of the copper current collector will reveal either the presence of a multitude of small holes (which are best observed by removing the remaining anode material and placing the current collector on a light table) or of pitting on the surface of the copper current collector as shown in Fig. H.19. Examination of the windings in cross section will show copper distributed throughout the anode, on the anode surface, and throughout the cathode material. Figure H.20 is an SEM image of a cell cross section (created by fracturing the electrode stack, which was embrittled during thermal runaway of a neighboring cell) with an overlaid x-ray map showing the distribution of copper. The cell in this image had been subjected to overdischarge and subsequently had partially burned. The observed redistribution of copper could only occur prior to the cell undergoing thermal runaway, and is thus a positive indicator that the cell had experienced severe and repeated overdischarge.

This effect had been seen earlier in lithium-sulfur dioxide primary cells after being driven into voltage reversal. These cells have a copper stripe current collector rolled into the lithium metal anode (see Chap. 14).

Figure H.18 Stereo-microscope image showing a hole in the copper current collector caused by overdischarge and copper dissolution. (Courtesy of Exponent, Inc.)
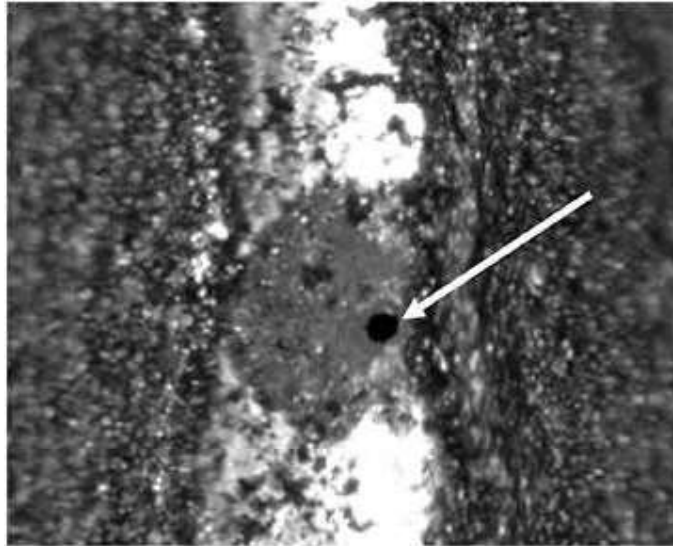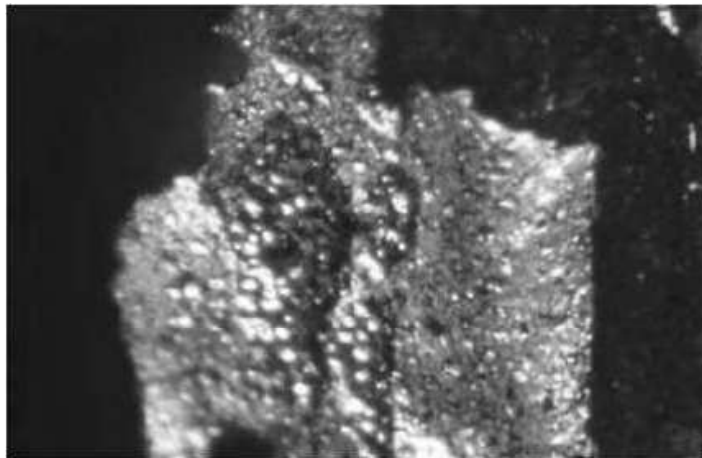

Figure H.19 Stereo-microscope image of pitting of the copper current collector surface associated with repeated severe over discharge. (Courtesy of Exponent, Inc.)


It is likely that cell shorting and thermal runaway, for incidents containing evidence of hard shorting (e.g., melted copper), develops through the following mechanism:

1. An initial shorting event as a result of a conductive path across the electrodes occurs that locally heats the copper current collector to its melting point of 1357 K.

2. Residual heat melts the separator near the point of shorting, creating a higher impedance short between anode and cathode active materials. The high impedance short continues to heat the cell, but the melting of the separator may interrupt or reduce the strength of the initial short and allow the melted copper to resolidify.

3. The high impedance short created between the anode and cathode by localized melting of the separator continues to heat the cell to the point where chemical reactions continue spontaneously (thermal runaway). During thermal runaway, the majority of the cell interior reaches a minimum temperature of 933 K, the melting point of aluminum.

4. In the final phases of thermal runaway, liquid aluminum may alloy with any exposed copper surface.

Figure H.20 SEM backscattered electron image of a D-size lithium-ion cell cross section (top) with a copper elemental map of the same region (bottom) showing copper dendrites growing through the separator from the negative to the positive electrode (between arrows). Cell cross-sectioning is discussed in the next section. (Courtesy of Exponent, Inc.)
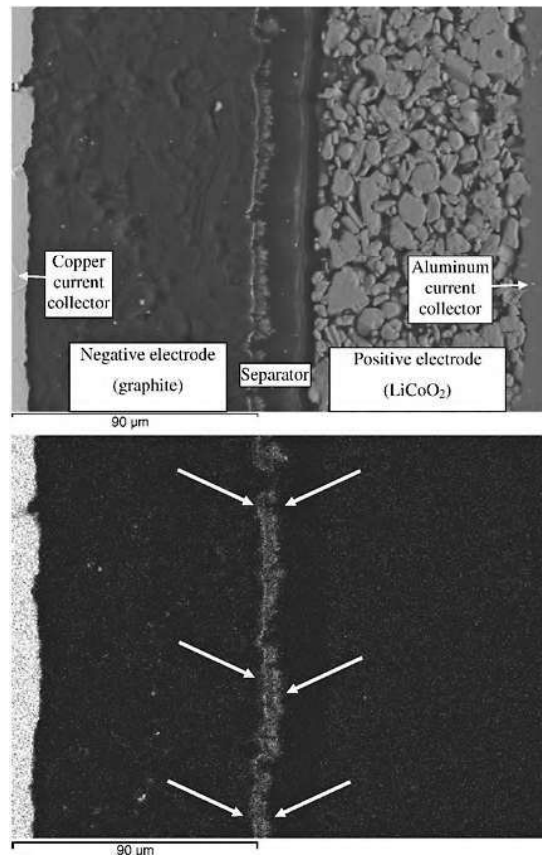
It should be noted that cell unrolling or destacking is not possible in many cases. Examples where such destructive physical analyses (DPAs) are difficult include:

Cells that are exposed to moisture while at high temperature because high temperature corrosion of the copper windings results in severely degraded and embrittled copper (e.g., if water was used to extinguish a fire).

Cells that are heated beyond the melting point of the separator and vented, but do not experience thermal runaway, so that the dried electrolyte and melted separator essentially glue the electrodes together (though subsequent baking may be possible to burn away the separator and allow further DPA).

Cells that experience violent gas generation and subsequent venting so that the windings are torn and tangled together in multiple locations.

Failure analysis of such cells depends more strongly on data obtained during analysis of the system electronics, and nondestructive analysis of the battery cells (x-rays, CT scans, etc.).

H.3.5. Cross-Sectioning

Another destructive examination approach for cells is cell cross-sectioning, which involves extracting the electrolyte and electrolyte-soluble components from the cell, followed by filling a cell with a polymer resin. The cell can then be physically cross-sectioned and prepared using nonaqueous polishing techniques to enable examination of the microstructure using optical and scanning electron microscopy (SEM) and energy dispersive spectroscopy (EDS). Cross-sectioning allows identification of electrode degradation, dendrite growth through the separators, manufacturing defects, and internal contaminants within the active materials that may not be visible otherwise. Unlike conventional techniques that require disassembly and harvesting of materials from a cell, the cross-sectioning technique preserves the electrode structure and the spatial relationship between the various components in the electrodes. Internal defects and degradation mechanisms, linked to safety, reliability, and performance problems, can be directly observed and characterized using this cross-sectioning technique.

Cross-sectional analysis of electrochemical cells has proven to be a successful technique in understanding degradation mechanisms in several battery systems, including lead acid,[25–32] nickel-metal hydride,[33,34] standard alkaline (Zn/MnO_2),[35] and lithium-ion.[36–42] For example, prior work on Zn/MnO_2 alkaline cells has shown that the analysis of polished cross sections can provide valuable information regarding the formation and spatial distribution of zinc oxide reaction products in porous electrodes. This information can be useful in determining if an alkaline cell was abused by attempted recharging, as shown in SEM images in Fig. H.21. These images were acquired from anode cross sections of three AAA Zn/MnO_2 alkaline cells. The image in Fig. H.21a shows the anode of an undischarged cell near the anode/separator/cathode interface. The bright gray spheres in the image are metallic zinc powder particles. The image in Fig. H.21b shows the same region of an anode from a cell that was discharged at 300 mA to 0.8 V. The zinc particles are noticeably smaller and surrounded by ZnO discharge product (dark gray). The same region of an anode from a cell discharged then recharged three times is shown in Fig. H.21c. In this image, smaller metallic zinc particles can be seen decorating the separator interface. These smaller zinc particles are the result of replating of zinc during recharging, and upon subsequent cycling become electrically disconnected from the rest of the anode.

An example of how cross-sectioning can be used to complement other techniques, such as CT scanning, is shown in Fig. H.22. In this example, a group of AA NiMH cells were found to be prone to high self-discharge rates and overheating during charge. Using CT scanning, large cracks were identified in the positive electrode, as shown in the CT slice in Fig. H.22a. An SEM image of a cross section of the cell in the same plane is shown in Fig. H.22b. Examination of the physical cross section enabled confirmation of the existence of the cracks in the positive electrode, and higher magnification imaging (Fig. H.22c) shows tearing of the separator where the negative electrode pushes into the void space left by the cracking in the positive electrode. The tearing of the separator resulted in multiple internal short-circuit locations and the high self-discharge rate and overheating observed with these cells.

Figure H.21 SEM images (backscattered electron contrast) showing axial cross sections of AAA alkaline anodes. The bright regions are metallic zinc powder particles. The darker gray regions (images b and c only) are ZnO discharge product. (a) New, undischarged anode; (b) discharged at 300 mA to 0.8 V; (c) cycled three times at 300 mA from 1.65 to 0.8 V. The effect of cycling on metallic zinc segregation toward the separator is evident in (c). (Courtesy of Exponent, Inc.)
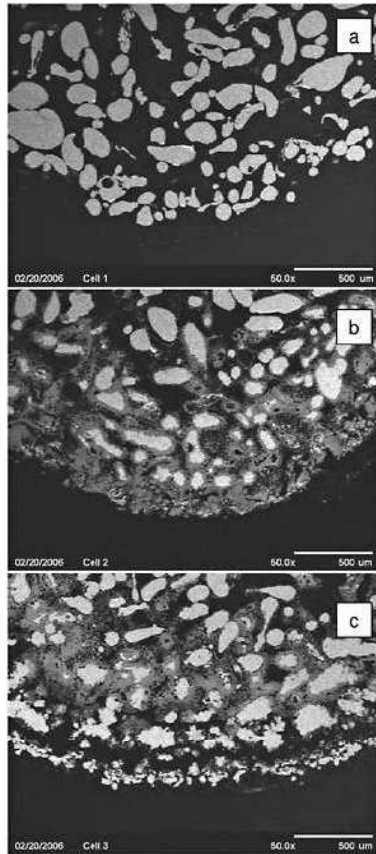
Figure H.22 *Analysis of physical cross sections can complement nondestructive techniques such as CT scanning. An axial CT slice of a new AA NiMH cell is shown in (a), where cracking within the positive electrode is clearly evident. SEM (backscattered electron contrast) is shown in (b) and (c) for the same cell. From these images, tears in the separator can be found associated with the cracks in the positive electrode. These tears in the separator were found to be the root cause of rapid self-discharging and overheating of the cells in some devices. (Courtesy of Exponent, Inc.)*
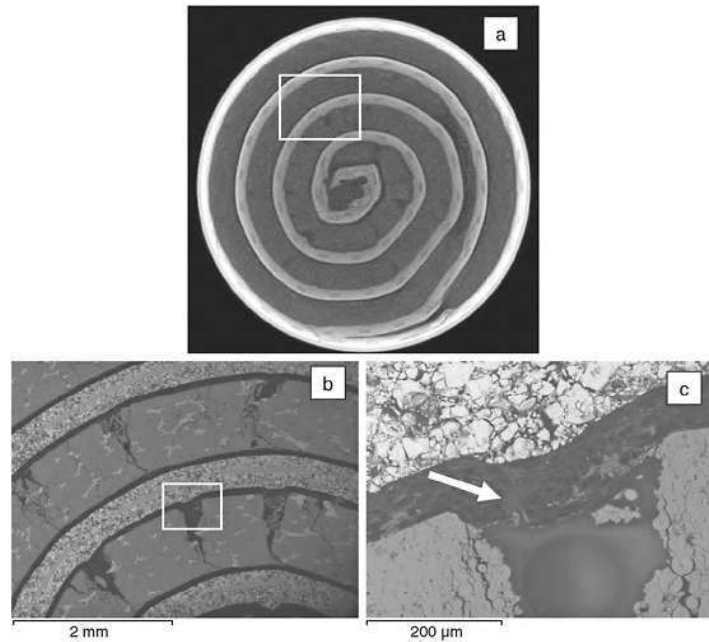
The cross-sectioning technique can also be used with lithium-ion cells, although great care must be taken to avoid potential safety issues related to rapid release of heat during the cross-sectioning process. With lithium-ion cells, it is important to ensure that all electrolyte has been extracted and that the cell is completely dry prior to impregnation with a polymer resin and physical cutting of the cell. A properly cross-sectioned lithium-ion cell can reveal valuable information about manufacturing defects, degradation mechanisms, and user abuse or misuse.

An example showing the effect of overcharging on the microstructure of an 18650 lithium-ion cell is shown in Fig. H.23. In this figure, the top two SEM images (*a* and *b*) show the microstructure of identical cells. The cell in the left image (*a*) was cycled between 3.0 and 4.2 V, whereas the cell in the right image (*b*) was cycled between 3.0 and 4.6 V. It is apparent that the negative electrode in the cell that was overcharged to 4.6 V is significantly thicker than its 4.2 V counterpart. In the carbon elemental maps shown below the SEM images (*c* and *d*), the presence of a gap can be seen between the graphite particles and the separator in the cell that was over-charged. The phosphorus elemental maps shown at the bottom of the figure (*e* and *f*) indicate that a thick, phosphorus-rich film is present at the graphite/separator interface of the overcharged cell. This phosphorus-rich film is consistent with an electrolyte reduction product that forms when metallic lithium is plated on the surface of the graphite when the cell is overcharged.

Figure H.23 *SEM images (a and b) and associated carbon (c and d) and phosphorus (e and f) elemental maps. Images on the left were obtained from an axial cross section of an 18650-size lithium-ion cell, whereas the images on the right were obtained from a similar cell that was overcharged to 4.6 V. The effect of overcharging can be seen at the interface between the negative electrode and separator, where a thick phosphorus-rich layer is found. This phosphorusrich layer is an electrolyte reduction product that forms from the reaction between metallic lithium and the electrolyte. (Courtesy of Exponent, Inc.)*
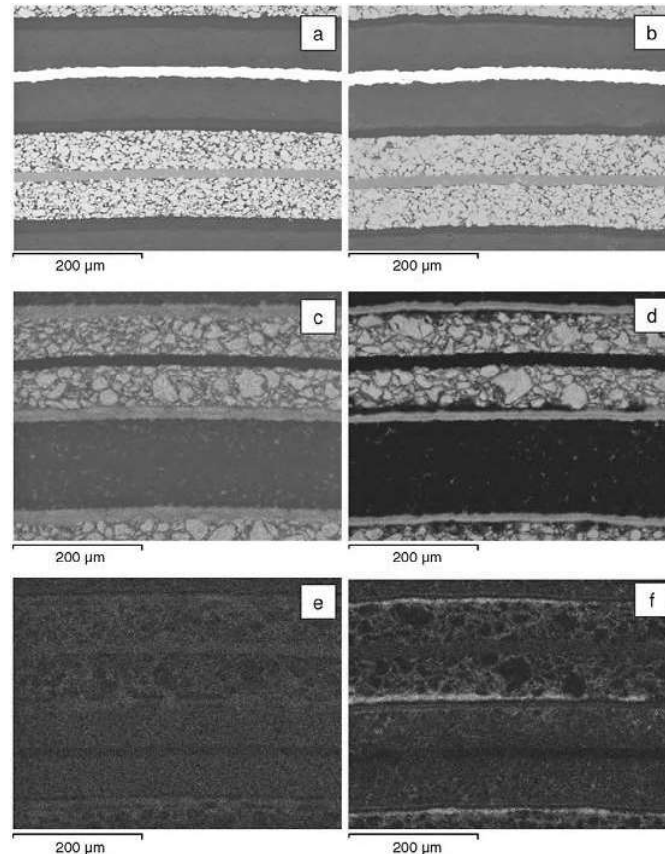
The cross-sectioning technique can also be useful for identifying internal microshorts in lithium-ion batteries. An example of this is shown in Fig. H.24 for high-power, 18650 lithium-ion cells that were prone to high self-discharge rates. In these cells, adhesive from Kapton tape on the positive electrode lead was in contact with delithiated Li_xCoO_2. Incompatibility between the adhesive and the delithiated positive electrode material resulted in dissolution of cobalt and the deposition of a cobalt-rich compound on the negative electrode, which bridged the separator and resulted in a high resistance internal short-circuit path in these cells. In Fig. H.24*b*, the intraseparator deposition can be clearly seen, and the elemental map in Fig. H.24 shows that this deposit is rich in cobalt.

As demonstrated in the above examples, examination of properly prepared cell cross sections can be a valuable tool in failure analysis, especially when used to complement other failure analysis techniques. However, as with any destructive technique used on batteries, care should be taken to prevent the introduction of contaminants, defects, and other sample preparation artifacts that might be misinterpreted by the investigator. In general, the investigator should be familiar with metallographic and materialographic sample preparation techniques, as well as the fundamental aspects of the design and construction of the cell being analyzed, in order to avoid misinterpretation of features observed in cell cross sections.

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Figure H.24 (a and b) Scanning electron microscope images (backscattered electron contrast) showing intraseparator deposits growing from the negative to the positive electrodes in a high-power 18650 lithium-ion cell. The area within the white box in (a) is shown at a higher magnification in (b). The cobalt elemental map in (c) shows that these deposits are rich in cobalt. Dissolution of cobalt from Li_xCoO_2 resulted from the use of an incompatible adhesive on Kapton tape on the positive electrode leads. (Courtesy of Exponent, Inc.)
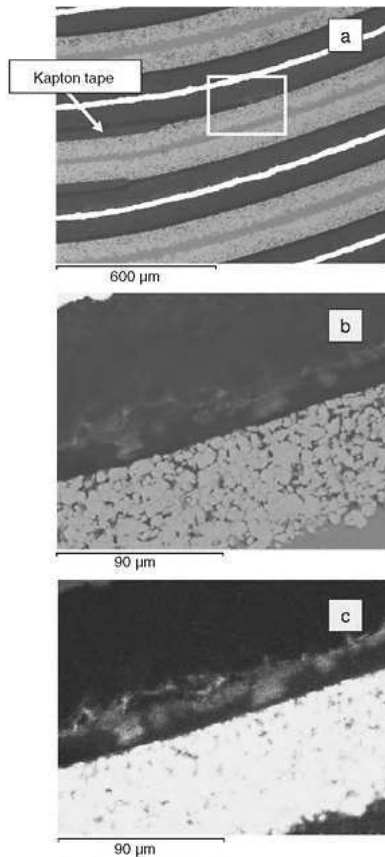
H.4. *BATTERY MANAGEMENT AND PROTECTION CIRCUITRY EXAMINATION*

Battery management and protection circuitry, which consists of the charger and often a battery protection PCB, is critical for safe and reliable battery operation with chemistries such as lithium-ion and in some cases, nickel-metal hydride, as well as for maximizing the useful life of the battery. Failure of battery pack protection circuitry to either sense or respond to an out-of-range condition can lead to failure of a battery. Assessment of the overall battery protection approach and examination of battery protection circuit components are important during any failure analysis. Failures, particularly of early generation systems, are occasionally the result of an oversight in the protection circuitry design that permits an unexpected out-of-range condition to be applied to a battery pack. For example, certain early notebook computer battery packs were susceptible to overcharge if used with some aftermarket general purpose battery chargers. Designers have since implemented charger/ battery pack identification "handshake" protocols that eliminate this failure mode. Obtaining system usage history is often useful in diagnosing such a flaw in the battery protection approach (e.g, was the system ever used with an aftermarket charger, fast charger, etc.).

Various battery chemistries require different levels of complexity in protection circuitry. Therefore, different levels of effort and understanding are required to diagnose any potential role of protection circuitry in a particular failure mode. Protection circuitry can require the monitoring of voltage, current, temperature, and/or pressure sensing for its effective operation. Aqueous battery systems often require simple protection electronics, while lithium-ion cells require complex protection systems. For example, in many simple household products and toys that use common alkaline batteries there are no electronic battery protection systems. Failures, should they occur (such as failure due to one or more batteries being inserted in reverse), tend to be mild in severity compared to more energetic failures that can occur with higher capacity batteries. In more sophisticated systems, with high-capacity batteries, high-rate batteries, and where multiple cells are assembled into series strings, the complexity of protection electronics increases. In some aqueous systems, a bimetal switch or thermal cutoff (TCO) is used to disconnect the battery in the case of battery overheating. Thermistors are utilized in some systems to provide feedback to a charger that can modify its state based on battery temperature. In large batteries, multiple thermally dependent devices and multiple voltage-sense lines located throughout the battery may be needed to adequately monitor, thermally manage, and protect the entire battery. These sensor components, their connections to protection circuitry, or the protection and management circuitry itself can fail resulting in battery failure. It is beyond the scope of this appendix to describe all possible permutations of protection electronics and their potential failure mechanisms. However, a basic description of the function of common protection and management elements, particularly those found in lithium-ion battery packs, is provided. An analyst should become familiar with the protection and management functions required by a specific battery chemistry, as well as how those functions are implemented in the particular battery design being examined. (See also Sec. 5.6.)

One of the most important functions of battery management and protection electronics is to manage and control charging (controlling charging rates and implementing appropriate charge cutoffs). Aqueous-based chemistries typically require their chargers to assert certain charging and hold profiles depending on the intended application of the battery. Automobile "starting, lighting, and ignition" (SLI) lead-acid batteries typically see charging and noncharging conditions a few times a day, and typically do not need to hold a charge for long periods of time. Uninterruptible power supply (UPS) devices need to assert charging after use and provide desulfation charge cycles (for lead-acid batteries) during their long-term standby state. Primary batteries need protection to prevent charging; typically a diode is used to prevent primary battery charging. Many systems actually implement two diodes for redundancy, *as single diode systems have been found to periodically suffer charging failures due to failure of a single diode.*

Another important function of battery management and protection electronics is to manage discharge. Many batteries are designed to provide high-rate capability. These batteries can provide significant current into an external short circuit that can then result in an overheating failure of components, circuits, or the battery itself. Therefore, high-rate batteries typically require protection against short circuit. This protection may be a simple fuse, a bimetal switch that opens when heated by excessive current, or more advanced protection in which a control circuit measures discharge current and opens a switch very quickly when a short-circuit current is sensed. Lower-rate batteries may safely limit short-circuit current with their own internal resistance and may not require short-circuit protection. Some batteries also require that discharge current be cut off once the battery voltage drops below a certain threshold. Lithium-ion batteries, for example, can be damaged by high-rate discharge currents when below approximately 3 V. These batteries are typically protected by electronics that open a switch to remove the load from the battery and terminate discharge at a specific voltage threshold. Many devices powered by batteries shut down on their own when their battery voltage drops below a threshold and therefore may not require a separate circuit for this function.

Lithium-ion batteries require relatively complex protection circuitry to protect against the following:

- *Charging to an excessive voltage.* Most lithium-ion batteries are rated to charge to 4.2 V. However, this maximum charge voltage varies depending on the specific battery chemistry or the intended use environment. Preventing overcharge is considered sufficiently critical to warrant individual monitoring of cell or series element (block) voltages by electronics to prevent any cell from exceeding a voltage limit. In addition, most electronic protection packages include multiple independent circuits to terminate charge so that a single-point circuitry failure cannot disable overvoltage protection.

- *Charging at an excessive current.* Most lithium-ion batteries are rated to charge at some fraction of their maximum cell charging rate. A safety margin is typically provided to account for aging of cells. In addition to being potentially detrimental to the cells, excessive currents can cause heating at connections both internal and external to cells, leading to undesirable effects.

- *Discharging at an excessive current.* High-rate discharges can cause heating of cells, in some cases to the point of damaging internal components such as the separator, and can lead to cell thermal runaway. For example, polymeric positive temperature coefficient (PTC) devices, also called resettable thermistor devices or "PolySwitches,"[*] are common components of commercial cells (e.g., part of the cap assembly of 18650 commercial cells) or commercial battery packs (placed in the circuits of battery packs designed with prismatic cells). These devices include a conductive polymer layer that becomes very resistive above some threshold temperature. PTCs are selected to remain conductive within specified current and temperature conditions. However, should discharge (or charge) current become excessive, the polymer will heat and become highly resistive, greatly reducing current from (or to) the cell. Once the PTC cools, it again becomes conductive.

- *Temperature excursions.* Charging lithium-ion batteries at low temperature can result in lithium plating due to reduced lithium-ion diffusion rates within the negative electrode. Charging or discharging lithium-ion batteries at high temperature can increase the risk of significant gas generation within the batteries, leading to swelling, the nuisance operation of pressure-triggered protective devices (e.g., CID: charge interrupt devices), or thermal runaway due to mechanical disturbance of windings or layers.

- *Imbalance protection.* Protection against the drifting of states-of-charge in cells connected in series. This protection may permanently disable a battery in which imbalance has become too severe, or may attempt to compensate for imbalance by equalizing cells using small discharge currents for cells at a higher state-of-charge. Batteries may not have imbalance protection and simply rely on overvoltage and undervoltage conditions to protect the battery. This can lead to early loss of battery capacity if severe imbalance conditions occur.

- *Discharging to excessively low voltage.* Lithium-ion batteries are mostly depleted when their voltage is below 3 V. Additional discharging, especially below 1 V, can cause damage to current collectors and ultimately to electrodes, leading to compromised performance or increased risk of thermal runaway. Thus, protection circuits tend to prevent discharge and themselves go into low-power sleep modes below certain voltages.

- *Precharge charging circuitry.* Lithium-ion batteries in a state of deep discharge require low charging currents until they reach a threshold voltage. Protection or charging circuitry is designed to charge at low rates until the desired voltage threshold is reached.

- *Additional passive thermally dependent protection devices.* These may also be integrated into a lithium-ion cell stack to protect against thermal runaway.

Protection circuitry tends to be simplified for a single-cell lithium-ion battery. The protection circuitry is typically integrated into a single protection printed circuit board (PCB) that achieves most or all of the protection functions discussed above. Some designs move some or all protection functionality to the host device rather than using a dedicated PCB in the battery.

Lithium-ion battery thermal runaway failures can cause significant damage to proximate PCBs. However, PCBs covered with heavy soot from a proximate battery failure often continue to function properly after the soot has been carefully removed. Additionally, most series connected lithium-ion battery protection PCBs have on-board nonvolatile memory. This memory is usually intact after a battery failure (even when the PCB appears heavily charred from the incident) and can provide important clues to the use pattern and environment the battery has experienced and to the root cause of the failure.

A lithium-ion battery protection PCB should be x-rayed in its as-received location prior to removal from the battery for evaluation separate from the battery. Once a protection PCB has been removed from a battery pack, it should be visually examined, x-rayed, and then cleaned. X-ray examination can reveal melting of copper traces that are generally associated with propagating PCB failures. Propagating PCB faults can heat nearby components and cells, potentially causing venting of cells or causing the cells to go into thermal runaway. X-ray images can also reveal the state of fuses, if present, which may be damaged from direct thermal exposure associated with venting of adjacent cells, or may signify an overcurrent failure within the PCB. A thorough discussion of propagating PCB faults and protection PCB evaluations is available elsewhere in Ref. 43.

Lithium-ion battery protection circuitry can also be a source of information about the pre-incident condition of the battery pack. As indicated above, some protection PCBs contain an EEPROM (electrically erasable programmable read-only memory) integrated circuit that stores data such as cycle count, remaining full charge capacity, and maximum temperature encountered by the pack, among other data depending on the complexity of the circuit. This information may prove useful for conducting a failure analysis of the pack. Data should be retrieved from the PCB, if possible, either by direct connection to the PCB if damage is minimal or by transplanting the EEPROM chip to an exemplar PCB and retrieving the information there.

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H.5. *WORKING WITH DATA FROM OEMS AND BATTERY MANUFACTURERS*

Involving the battery pack assembler and cell manufacturers in an investigation increases the likelihood of determining failure cause(s) and identifying potential problems that may be associated with a certain production time line. The battery pack and cell manufacturers should be able to examine production data from around the time of the failed battery production and report any abnormally high reject rates, manufacturing changes, supplier changes, or production rate upsets. Of particular interest in lithium-ion battery failure analyses are the failure rates of high potential (HiPot) and open-circuit voltage (OCV) tests, and any investigations of cells that failed these tests.

Manufacturers often retain production sample batteries from each batch or a selection over a period of time, so they may have sample batteries from times consistent with failed batteries and may be able to provide these batteries for examination. As a theory of the failure mode develops, the manufacturer should be able to describe relevant manufacturing processes so an understanding can be developed of how a particular type of fault could have occurred and the likelihood of additional field failures.

Manufacturers may have access to batteries returned from customers as a result of any number of nonenergetic failures (e.g., a battery simply stopped working, had a prematurely reduced capacity, etc.). Examination of batteries from an incident battery lot (and similar lots) can prove invaluable, even if the exemplar batteries show no obvious symptoms of failure. Catastrophic battery failures are typically a result of multiple failures that align to create a perfect failure condition. Field returned batteries manufactured at similar time frames as incident batteries may very well have less severe manifestations of similar failure modes. Examinations of these cells can yield an understanding of one or more failure modes that might be required for catastrophic failures (incidents) to occur. Examination of such field returns can be conducted using a combination of the techniques described above, including CT scanning, cycling, electrochemical testing, cell disassembly, or cell cross-sectioning.

With multiseries lithium-ion cells, some battery field returns result from pack protection electronics driving a permanent disabling of the battery pack. Protection electronics permanently disable the pack for a number of reasons, including diverging voltages between series elements (blockimbalance), block overcharge, over-rate charge, over-rate discharge, etc. If some battery packs from a given production lot fail in an energetic manner, it is likely that a number of other packs from the same lot will fail relatively benignly after the protection electronics disables the packs. Thus, examination of permanently disabled packs from a suspect lot can be particularly useful in developing a failure mode hypothesis for any energetic failures from that lot.

Statistical analysis of battery pack failure rates is often necessary to determine whether a collection of battery incidents indicates a batch of batteries with an elevated failure rate. If a batch or a series of batches of batteries with an elevated failure rate can be identified, it is possible to recall batteries from that batch and replace them with cells that should[*] have a lower failure rate. The decision to consider a recall depends on several factors in addition to the actual expected failure rate, including the type and severity of the failure mode, the likelihood of potential harm to people, and damage to property. Statistical modeling can help determine whether observed failures are "infant mortality failures" or if there is an underlying failure rate over time. It can compare different contributing factors that may be identified in the course of discussions with battery manufacturers to determine whether they may or may not have a statistically significant relationship with the failure rate. This can help rule out certain factors as possible contributors to the actual incidents and limit potential recall populations. Statistical analysis can also predict, within a certain confidence interval, the number of expected failures in the future so the remaining risk is known if it is decided a recall is unnecessary.

H.6. *CONCLUSIONS*

Any failure can be investigated effectively through application of the scientific method:

1. Collection of observations and evidence

2. Development of an hypothesis

3. Testing of the hypothesis

This appendix described a number of techniques that can be used as part of the investigative process. Many of the techniques described here have proven useful in examining failures of lithiumion batteries, lithium primary batteries, nickel-metal hydride batteries, as well as batteries of other chemistries. This appendix is not an exhaustive description of all failure analysis techniques that can be applied to examine battery failures, and many additional techniques commonly employed by electrochemists, mechanical engineers, electrical engineers, and chemical engineers can be considered for approaching battery failures. Additionally, the techniques and conclusions presented in this appendix are intended as guidelines on how to approach a battery failure analysis. A battery failure investigation may not require the use of all the techniques discussed here. Furthermore, it should be noted that each battery failure is a unique case and thus requires a unique combination of various investigative strategies and techniques that should be tailored for that specific investigation accordingly.

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[*] A block is a parallel array of cells. Multiple blocks are often combined in series.

[*] The cell system consisted of a $LiCoO_2$ positive electrode, graphite negative electrode, and electrolyte comprised of 1 M LiPF dissolved in a mixture of ethyl methyl carbonate, diethyl carbonate, dimethyl carbonate, and ethylene carbonate.

[*] The observed brightness is set by the operator and can only be used as a qualitative comparison relative to other materials that appear in the same image.

[*] PolySwitch is a trademark of Tyco Electronics.

[*] A new cell batch will actually have an unknown failure rate, so recall decisions must weigh the risk that the replacement cells may have a higher failure rate than those being replaced. For example, if a group of failures can be shown to be part of an "infant mortality group," and other cells from the batch have been in the field long enough, leaving unfailed units in the field may be safer than replacing them with other units of unknown failure rates.